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DETONATION CHEMISTRY: AN INVESTIGATION
OF FLUORINE AS AN OXIDIZING MOIETY
IN EXPLOSIVES.

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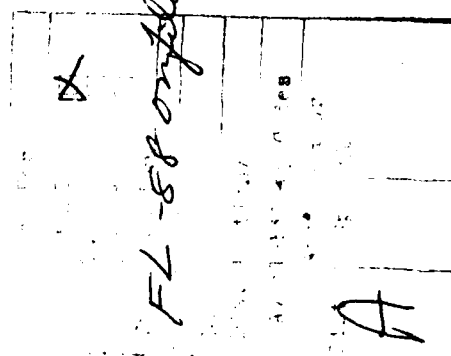
DETONATION CHEMISTRY: AN INVESTIGATION OF FLUORINE AS AN
OXIDIZING MOIETY IN EXPLOSIVES

R.R. McGuire, D.L. Ornellas, F.H. Helm, C.L. Coon, and M. Finger
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were designed and built
This report *was prepared* *were then written.*
We have investigated the use of fluorine in the form of the difluoramino (NF_2) group as an oxidizing moiety. Bis- and tris-difluoramino perfluorobutane, previously unknown, were especially synthesized for this study. We performed detonation calorimetry to determine the exact detonation product composition and the heat of detonation of a series of NF_2 compounds and mixtures. We then performed cylinder tests to determine their detonation performance. Similar tests on NO_2 compounds were used for comparison. For reasons of toxicity and safety, we designed and built remote mixing and loading apparatus for certain of the materials. Materials were chosen to highlight certain of the detonation products. Hydrogen fluoride was found to be a favorable detonation product compared with H_2O , CO_2 outperforms CF_4 at all cylinder expansion ratios, and Al_2O_3 was a favorable detonation product compared to AlF_3 . The most important result is the better understanding of the mechanism of reaction of small-particle aluminum in a detonation.

INTRODUCTION

A detonating high explosive or monopropellant can be viewed both as a potential combination of fuel and oxidizer and as potential energy ("Q" source) and a potential working fluid (detonation or combustion products). The goal, within practical safety limits, is usually to maximize "Q," i.e.,



the difference in the free energies of formation between the explosive or propellant and the detonation or combustion products. Furthermore, for an explosive, the characteristics of the expansion adiabat are determined by the temperature and composition of the detonation product gases.[1]

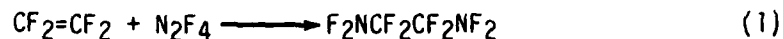
There is very little difference between oxygen and fluorine as oxidizing moieties from thermodynamic considerations. (Fig. 1) Despite this, there has been very little, if any, effort to investigate fluorine as an oxidizing moiety in explosives. By far, the most widely investigated oxidizing species is oxygen, usually attached to nitrogen, i.e., $-\text{NO}_2-$, $-\text{ONO}_2$, NO_2- , NO_3- , etc. All of the common explosives and propellants (certain primary explosives excepted) contain some form of oxygen carrier, e.g., nitrate, perchlorate.

In this investigation, we compare the expansion isentropic performance of oxide and fluoride detonation products. Thus we compare water (H_2O) with hydrogen fluoride (HF), carbon dioxide (CO_2) with carbon tetrafluoride (CF_4), and aluminum oxide (Al_2O_3) with aluminum fluoride (AlF_3). The explosives used in the investigation (Table 1) were formulated for this purpose and are, generally, of little practical interest.

EXPERIMENTAL

Synthesis of perfluorinated alkylamines

Because one of the objectives of the investigation was to determine the performance of CF_4 and AlF_3 as detonation products, we wished to use explosives which would give as few additional products as possible. Difluoramino compounds were the logical choice for explosives with sufficient energy and reasonable physical properties. Several of these compounds were synthesized. Perfluoroethylene diamine ($\text{F}_2\text{NCH}_2\text{CH}_2\text{NF}_2$) was chosen as a test compound and synthesized by the addition of N_2F_4 to the tetrafluoroethylene, eq. (1).



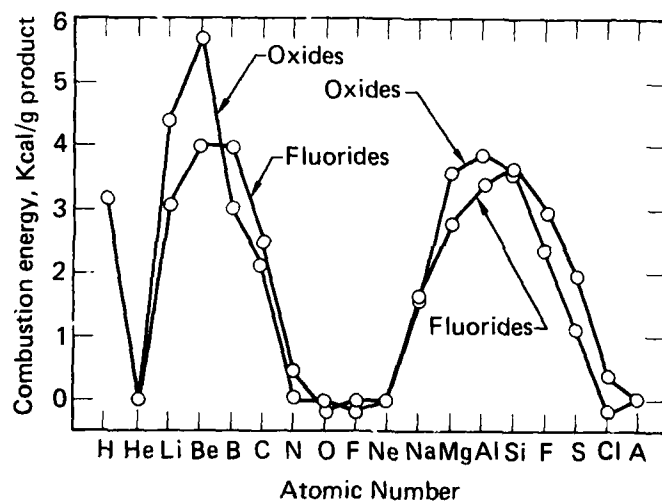


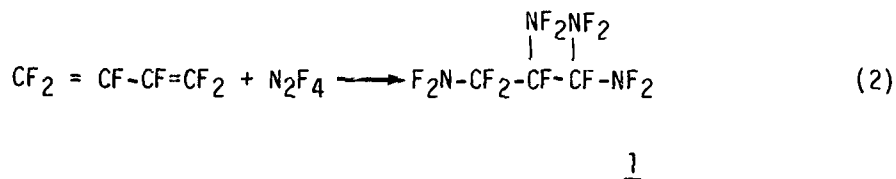
Fig. 1. Combustion Energies of the Elements.

Table 1

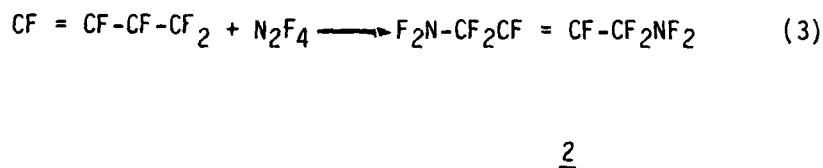
<u>Explosives used to investigate isentropic behavior</u>	
<u>Product</u>	<u>Explosive</u>
H ₂ O	RX-23-AA (78.42 wt% hydrazine nitrate, 21.58 wt% hydrazine) RX-23-AB (69.02 wt% hydrazine nitrate, 5.08 wt% hydrazine, 25.90 wt% water)
HF	1,2-bis(difluoramino)propane (1,2-DP)
CO ₂	Hexanitrobenzene (HNB)
CF ₄	A mixture of bis and tris (difluoramino) perfluoro butanes (BDFPB and TDFPB). The mixture is designated PFB.
Al ₂ O ₃	67.7 wt% tetranitromethane with 32.3 wt% aluminum (balanced to Al ₂ O ₃ , N ₂ , and C)
AlF ₃	74.7 wt% of the mixture of difluoramino perfluorobutanes with 25.3 wt% aluminum (balanced to AlF ₃ , N ₂ , and C)

N_2F_4 reacts with perfluoroethylene under pressure at about 100°C to give good yields of octafluoroethylene-diamine.[2, 3] We repeated this work on a small scale and were able to prepare 2.0g of octafluoroethylene diamine. Scale-up of this reaction to a 40-g resulted in a serious explosion and loss of the autoclave and other equipment required for this work. Subsequently, we consulted with other chemists who have prepared this compound but who have not recorded their experiences and results in the literature such that their findings are readily accessible. Specifically, discussion with Dr. Ralph Davis of Dow Chemical Company, Midland, Michigan, revealed that explosions in reactions involving N_2F_4 and olefins are not predictable or uncommon. In addition, the boiling point of the product, perfluoroethylenediamine (6°C), required difficult and expensive, low-temperature handling techniques during subsequent testing. Consideration of these points led to a choice of a higher boiling CNF explosive.

To obtain a higher boiling product, we attempted the preparation of 1,2,3,4-tetrakis(difluoramino)-1,1,3,4,1,-hexafluorobutane, 1, by the addition of N_2F_4 to hexafluorobutadiene:



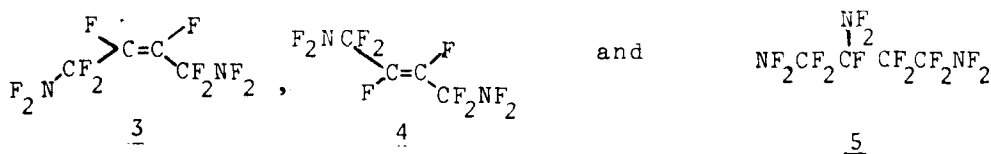
Although the preparation of 1 had not been reported, the reaction of N_2F_4 with polyfluorobutadiene was reported to give only the 1,4 addition product, 2, Eq. (3).[4] We felt that under more vigorous reaction conditions a second molecule of N_2F_4 could be added to the double bond of 2 to give 1.



A series of reactions was run in which perfluorobutadiene was combined with slightly more than two molar equivalents of N_2F_4 in an autoclave cooled to $-78^\circ C$. Mixing of the two starting materials was imperative before allowing the mixture to warm to ambient temperature to avoid violent exothermic decomposition.

The desired quantities of perfluorobutadiene and N_2F_4 are alternately condensed in thin layers into the autoclave. This layering of the two starting materials before the autoclave is heated is imperative to avoid violent exothermic decomposition of both starting materials. After both starting materials are in the autoclave and mixed, the system is heated to between 120° and $180^\circ C$ for 10-30 hours. The autoclave is cooled to ambient temperature and the light-blue liquid product analyzed.

The composition of the product from the reaction of N_2F_4 and perfluorobutadiene was relatively constant over a temperature range of 120° - $180^\circ C$ and a N_2F_4 /perfluorobutadiene ratio of 2/1 to 5/1. The product mixture was composed of three major products which were identified as:



The structural assignments were confirmed when pure samples of these components, isolated by preparative chromatography, were analyzed by ^{19}F NMR spectroscopy and mass spectroscopy.

The assignments are based on the following data: the two most volatile products are geometric isomers since their IR spectra and mass spectra are nearly identical. The ^{19}F NMR spectrum of the most volatile component showed three different fluorine atoms present in the molecule, $-\text{CF}_2-$, a $-\text{CF}-$, and $-\text{NF}_2$. If the spectrum was run while the $-\text{CF}_2-$ group was irradiated and decoupled from adjoining fluorine atoms, the splitting pattern for the $-\text{CF}-$ group was reduced from a complicate multiplet to a triplet.

These observations are consistent with the linear product, 2. Decoupling of the $-CF_2-$ group in 2 would be expected to give a triplet for the $-CF-$ caused by long-range splitting by the $-NF_2$ group and a doublet for the $-NF_2$ group. Both of these splitting patterns were observed. The resistance of 2 to the addition of N_2F_4 across the 2,3- double bond is not fully explained but might be attributed to the electron withdrawing character of the fluorine atoms and the difluoramino group.

The higher boiling component of the reaction mixture, 5, was shown by ^{19}F NMR analysis to contain three $-NF_2$, three $-CF_2-$, and one $-CF-$ group in a linear molecule. Only one structure can be suggested that meets these criteria and that is 1,2,4-tris- (difluoramino)-1,1,2,3,3,4,4-heptafluorobutane, 5. Decoupling experiments also support this conclusion. The mechanism for the formation of 5 has not been determined, but it can be suggested that N_2F_4 first adds either 1,4- or 1,2- to perfluorobutadiene. Then NF_3 , which is known to form from the decomposition of N_2F_4 at the temperatures used for this reaction, adds to the remaining double bond.

The separation of the reaction products is accomplished at ambient pressure. The two lower boiling components, the cis and trans isomers of 2, boil at $58-60^{\circ}C$. The higher boiling component was purified by distillation at $54-55^{\circ}C$ at 200 mm Hg.

A 100.8-g sample that was 90% 2, 8% 5, and 2% other fluorinated impurities was supplied for detonation calorimetry tests. A 10.33-g sample that was 92% 5 and 8% 2 was also included.

Detonation Calorimetry - Apparatus

Figure 2 shows the calorimeter used for these measurements. The spherical bomb, made of 3.2-cm-thick 347 stainless steel or, if HF-producing explosives are used, is 400 Monel. It has an i.d. of 21.6 cm and an internal volume of 5.28 litre. The 9-cm opening is covered by a lid 3.8-cm thick at the center. The lid is secured by 12 1-cm diameter stainless steel bolts inserted through the lid flange and is sealed with a Neoprene O-ring. The bomb and lid weigh 52 kg.

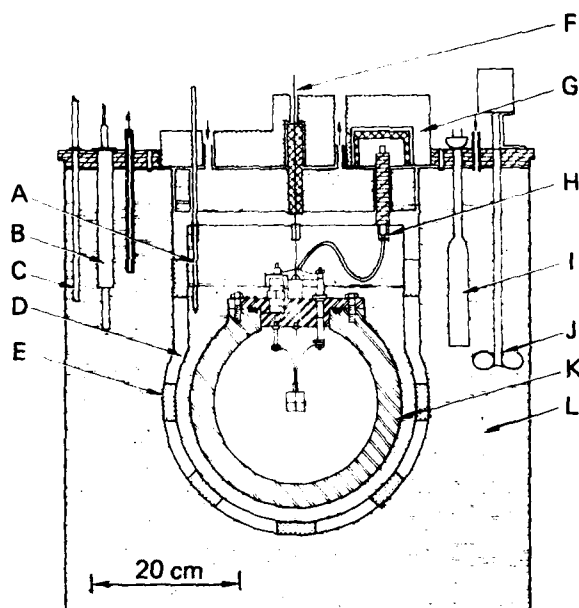


Fig. 2 Calorimeter; A-Quartz thermometer probe; B-Nickel thermometer; C-mercury in glass thermometer; D-calorimeter bucket with lid; E-Styrofoam support blocks; F-support cable; G-Styrofoam insulation; H-firing lead connector; I-knifeblade heater; J-stirrer; K-bomb; and L-constant temperature jacket.

The bomb is suspended by a 0.16-cm braided steel cable in a polished stainless steel calorimeter bucket that holds 8.4 kg of water; the water is stirred by vertical oscillations of the bomb. The bomb and spherical portion of the calorimeter bucket are separated by 1.8 cm of water. The water temperature is sensed by a quartz thermometer probe.

The calorimeter is surrounded by a constant-temperature jacket with a jacketed lid. An insulated firing-lead connector is mounted through the bucket lid and extends through a well in the jacket lid. The constant-temperature jacket is maintained at $25.000 \pm 0.001^{\circ}\text{C}$ by a temperature controller that senses the temperature with a nickel resistance thermometer and heats with a knifeblade heater. A small centrifugal pump circulates water from the jacket through the jacket lid.

The thermometric system is a Hewlett-Packard Model 2801A quartz thermometer with a sensitivity of 10^{-4}°C for differential measurements. It has direct digital readout and is easily calibrated. The thermometer is interfaced to a Digital Computer Controls, Inc., D-112 computer [5]

We determined the energy equivalent of the system by burning about 5.9 g of benzoic acid (certified by the National Bureau of Standards) with purified oxygen at a pressure of 30 atm in a platinum crucible. The benzoic acid was pressed at 140 kg/cm^2 into a pellet 2.54 cm in diameter and about 1.3 cm high. The 0.05-cm-thick crucible was suspended centrally in the bomb. Fifteen ml of water was placed in the bomb to conform with standard benzoic acid calibration conditions. The benzoic acid was ignited by an electrically heated 14-cm length of 0.015-cm-diameter pure iron wire. The heat input from benzoic acid was corrected to standard states.[6] Total corrections amounted to 0.01%. The equivalent of the instrument, taken as the average of six calibration runs, is $15,200 \pm 4 \text{ cal}^{\circ}\text{C}$. This error of $\pm 0.03\%$ indicates the ultimate precision of the instrument.

Detonation Calorimetry - Procedure

The experimental arrangement used for this investigation has been described in detail [7]. The charge, confined in a gold cylinder, is suspended by two gold straps attached to the lid. Gold wires tightened around the straps and the gold cylinder hold the cylinder in place on bent ends of the straps. The confining cylinder is closed on both ends and extends a distance of one charge diameter beyond both ends of the charge. (Explosive charges are typically 12.7 mm in diameter and 114 mm long.) The confining cylinders have a wall thickness equal to the charge diameter. The bottom of the cylinder is closed to preclude jetting.

To contain the liquid explosives under vacuum conditions, we sealed the gold cylinder 12.7 mm from the top end with a translucent laminate film of 0.025-mm polyethylene and 0.013-mm Mylar. A vacuum-tight seal was obtained by compressing the film between appropriately machined gold surfaces. The weight of film averaged 0.017 g per experiment. The bottom of the gold cylinder was sealed by electron-beam welding the gold plug in place. A gold fill tube 2.03 mm OD and 0.75 mm ID was soldered through the cylinder wall as near as possible to the film seal. Liquids were loaded through this tube with a syringe. The tube was sealed by cold welding.

Detonators were specially fabricated from inert components, i.e., gold bridgewires and cups, platinum leads, and alumina headers. About 100 mg of powdered PETN was packed around the bridgewire in the detonator cup and a 150-mg high-density (1.71 g/cm^3) pellet of PETN placed next to the main charge. In some cases, the face of the gold cup was removed so that the high-density pellet was in direct contact with the main charge. Because of differences in the initiation characteristics of the explosives studied, boosters of various sizes were sometimes required. Boosters were made of PETN with a density of 1.71 g/cm^3 , and their weight was kept to a minimum. The heat and products of detonation of each explosive were corrected for the PETN used in the detonator and booster.

Before firing the explosive, the bomb was evacuated to a pressure of about 50 μ m Hg. To avoid splashing of the water in the bucket, firing was initiated when the bomb was at the bottom of its stirring stroke. Detonators were fired with a 6.72 μ F-2400 V capacitance-discharge unit.

A vacuum system was built to measure total volume of gaseous detonation products and to permit the taking of samples. To help remove the gaseous detonation products, the bomb is heated to 100°C at the end of the transfer. Water was condensed in two in-line traps at -95°C and determined gravimetrically. Ammonia that is not retained in the water traps reacts with sulfuric acid in a third trap.

The remaining gases are pumped into a calibrated 35-litre stainless steel tank where the pressure and temperature were measured. The tank contains small Teflon spheres that assure complete mixing of the gases when the tank is tumbled. Carbon dioxide, carbon monoxide, nitrogen, hydrogen, methane, and carbon tetrafluoride are determined quantitatively by mass spectrometry as are the trace quantities of other products.

While the bomb is still hot, the interior is washed with water. Ammonia is determined by wet analyses of the two water traps, the sulfuric acid trap, and the bomb washings. Hydrogen cyanide is determined by wet analyses of the water traps and bomb washings. Small amounts of CO₂ and occasionally, depending upon the explosive, nitrite ion (NO₂⁻) and nitrate ion (NO₃⁻) are found in the water traps and bomb washings; these species are determined by wet analyses.

For explosives that produce hydrogen fluoride and little or no water, two traps for HF and water having either polyethylene or Kel-F residence areas and made with Monel valves and tubing are substituted for the glass water traps. Both traps contain potassium fluoride that is prepared by heating in air at 475°C. These traps are held at -130°C during the gas transfer. The HF is determined by wet analysis of the contents of these traps and the Monel bomb washings.

The solid products that are water insoluble--silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), carbon (C_s), and aluminum trifluoride (AlF_3) remain in the bomb. The first three are amorphous and are determined by difference using the material balance. The presence of SiO_2 was established by infrared spectroscopy. AlF_3 was determined by x-ray fluorescence.

High-density charges of hexanitrobenzene were pressed as right cylinders in mechanical dies at pressures of 1000-2000 kg/cm^2 , without vacuum at ambient temperature to give densities of about 95% of TMD. Pressed pieces are 12.7 mm long. PFB (BDPFB-TDPFB), RX-23-AA, and RX-23-AB were liquids that were loaded into the gold cylinder in the liquid configuration in a contact operation using a syringe as describe above. TNM/Al was a paste of whipped-cream-like consistency that was loaded into the cylinder with a spatula in a contact operation with the cylinder mounted on a vibrating table so as to remove air pockets. When the cylinder was full, it was sealed with the polyethylene-mylar film as described earlier. 1,2 DP, a liquid, and PFB/Al, a paste, were too impact sensitive to be handled in contact operations. The procedure for PFB/Al will be described in detail as an example of how complex the remote mix, fill, and closing of a calorimeter experiment can be.

The PFB/Al experiment presented several interesting challenges. First the PFB/Al mixture proved to be very impact sensitive, with drop weight hights ranging from 2 to 9 cm, depending on conditions. Secondly, the PFB explosives were highly volatile which mandated certain design and operational criteria. BDFPB had a density of 1.63 g/cm^3 and boiled at about 59°C while TDFPB had a density of 1.77 g/cm^3 and boiled at about 70-75°C. Both had high vapor pressures at room temperature. Their mixture, even though sealed, changed composition with time. Lastly, the aluminum loading of 25.3 wt% was too low to make a stable paste, as we were fortunate to obtain in the TNM/Al experiment.

We used a mock paste for all tests to develop hardware and procedures. It consisted of $\text{CCl}_4/\text{Al}/\text{SiO}_2$ -74.2/24.5/0.75 wt%. CCl_4 was chosen as a mock because its density of 1.59 g/cm^3 and boiling point of 77°C were reasonably close to those for the PFB explosives. However, it had the disadvantage of a lower vapor pressure at room temperature which led us to a false sense of security in the tests leading up to the live experiment.

The aluminum used was Alcoa 1660, a powder consisting of very thin flakes, designed for the explosives industry. The average particle size, based on surface area measurements, was $0.5 \mu\text{m}$. The flakes ranged from 3-65 μm on the flat side. This material analyzed 86.5 wt% active aluminum, 2.77% stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$) and an assumed 10.73 wt% Al_2O_3 by difference.

A series of mock pastes were made in which the cab-o-sil (SiO_2) content was 0.5, 0.75, 0.825, and 1.0 wt%. They were allowed to stand overnight and inspected for evidence of setting. The paste with 0.75% SiO_2 resulted in a stable gel.

Another series of tests showed us that the best way to load the 0.635 cm diam. by 14.6-cm long shot cylinder was to premix the paste and load it through 1.4 mm ID gold tubing we had available. It was necessary to vibrate the cylinder with high frequency and low amplitude to cause the gel to flow down the cylinder wall and fill from the bottom up. When filled, the paste exits through an overflow tube at the very top of the cylinder and becomes visible in a bubbler vial. An alternative method of filling that proved to be unsuccessful was to pack the cylinder with a dry mixture of aluminum and SiO_2 and inject the PFB liquid into the powder from the bottom of the cylinder.

Another test showed that pinching and cold welding shut gold tubing loaded with live explosive would not result in a detonation in eight trials.

Figure 3 is a schematic of the remote mixing and fill apparatus. Figure 4 shows this equipment in a remote cell and includes the hardware, not shown in Figure 3, to remotely close and seal the calorimeter bomb. Figure 5 is a close-up of the bomb lid, shot cylinder, detonator, and cold welding device. Figure 6 shows the mixing container, a 20 cm³ plastic syringe with a special teflon piston and sealing tip, and the super mixer which vibrates the syringe to mix and deaerate the paste.

The general arrangement is as follows: The gold shot cylinder is pre-positioned, supported by gold straps attached to the calorimeter bomb lid. The lid is held in the open position by an air cylinder. The EBW detonator is connected to the high voltage feedthrough and the grounding terminal which are shorted by clip leads at the top of the lid. The detonator is in place in the top of the gold cylinder. Fill and overflow tubes lead outward from near the top of the cylinder and pass between the open jaws of the cold welding device. Polyethylene tubing connected to the overflow tube leads to a bubbler which shows that the paste is flowing during the filling operation. Figures 3, 4, and 5 show the hardware, either air or electrically operated (67 volts DC), to remotely remove the syringe plug, drive the syringe piston, weld tubing, remove the cold welder from under the bomb lid, lower the lid with the bolts in place, move the electrically driven socket over the bolt, lower the socket onto the bolt, snug up the bolts, and rotate the bomb to the next bolt position.

At every step of the procedure provisions were made for possible malfunctions. During all contact operations the operator wore a flak vest, a heavy duty face shield, ear protection and rubber gloves. All operations in which the explosive was subjected to work or friction were remote.

Weighing of the explosive components into the plastic syringe was done within the remote cell, adjacent to the apparatus, to minimize the distance the explosive mixture had to be moved and the potential for dropping. The liquid PBF explosive was added last from a plastic syringe. The mixing syringe was immediately sealed with the Teflon tip to avoid evaporation of the liquid PFB.

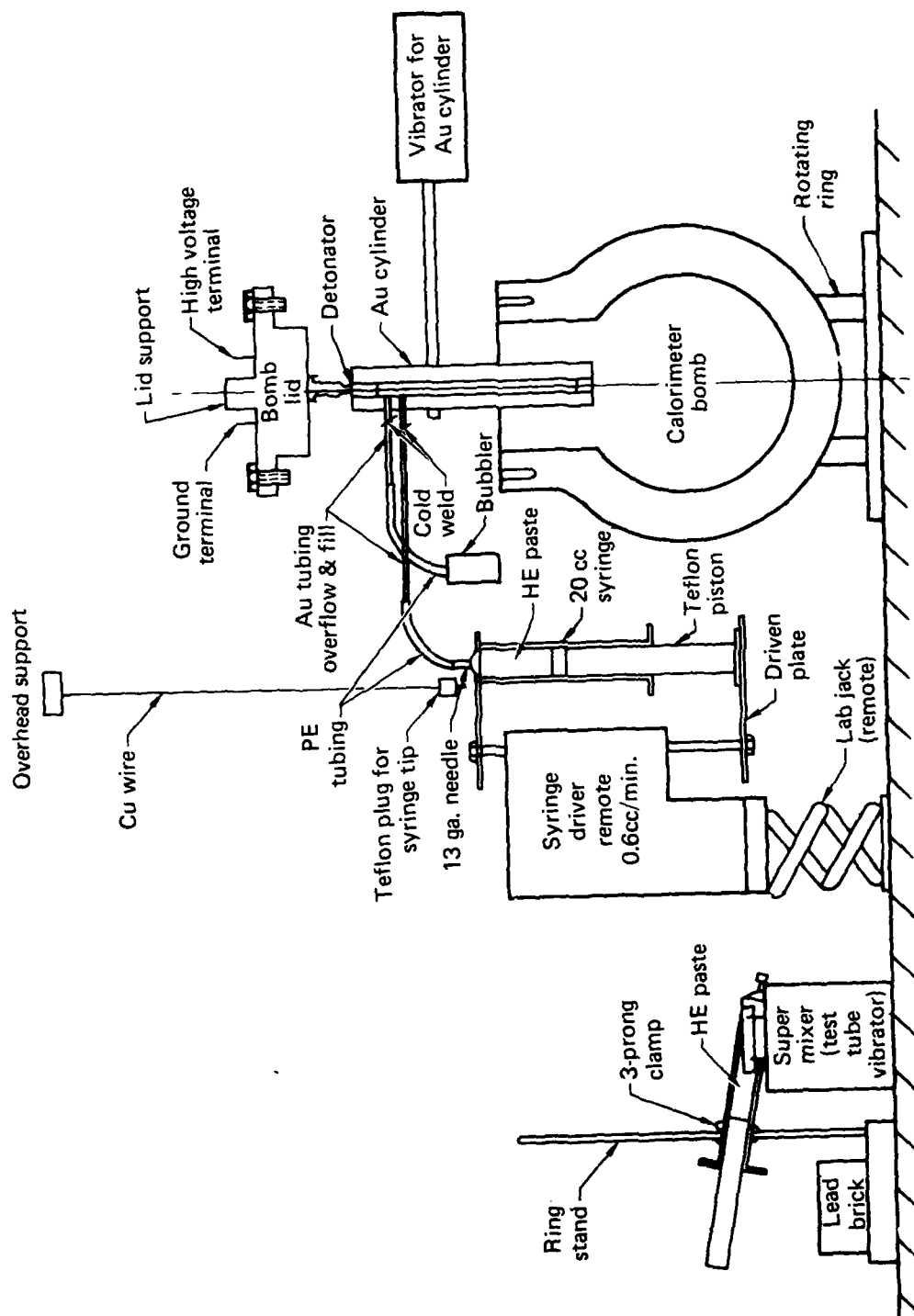


Fig. 3. Mixing and fill system for PFB/A) experiment.

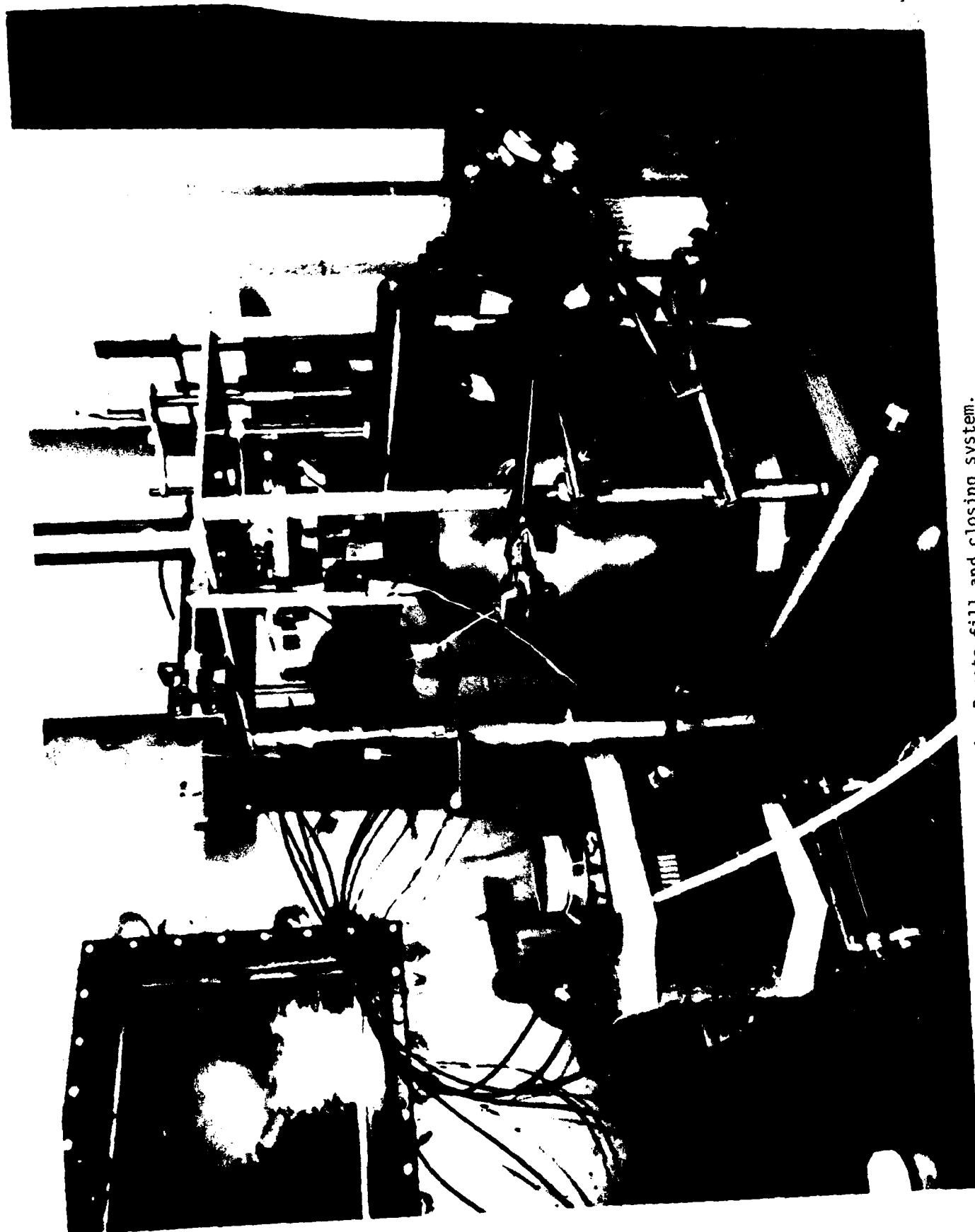


Fig. 4. Remote fill and closing system.

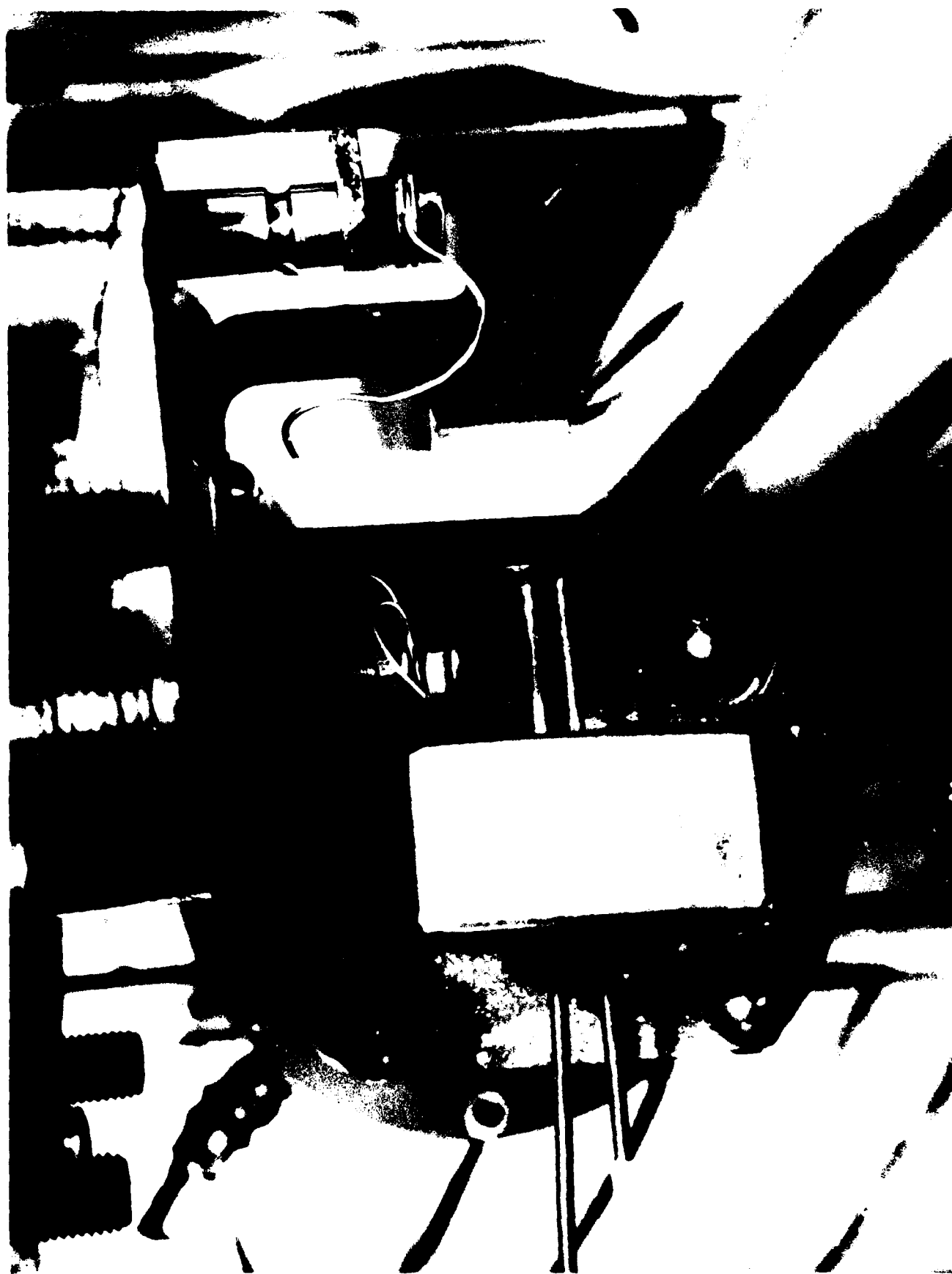


Fig. 5. Calorimeter bomb lid and cold welding device.

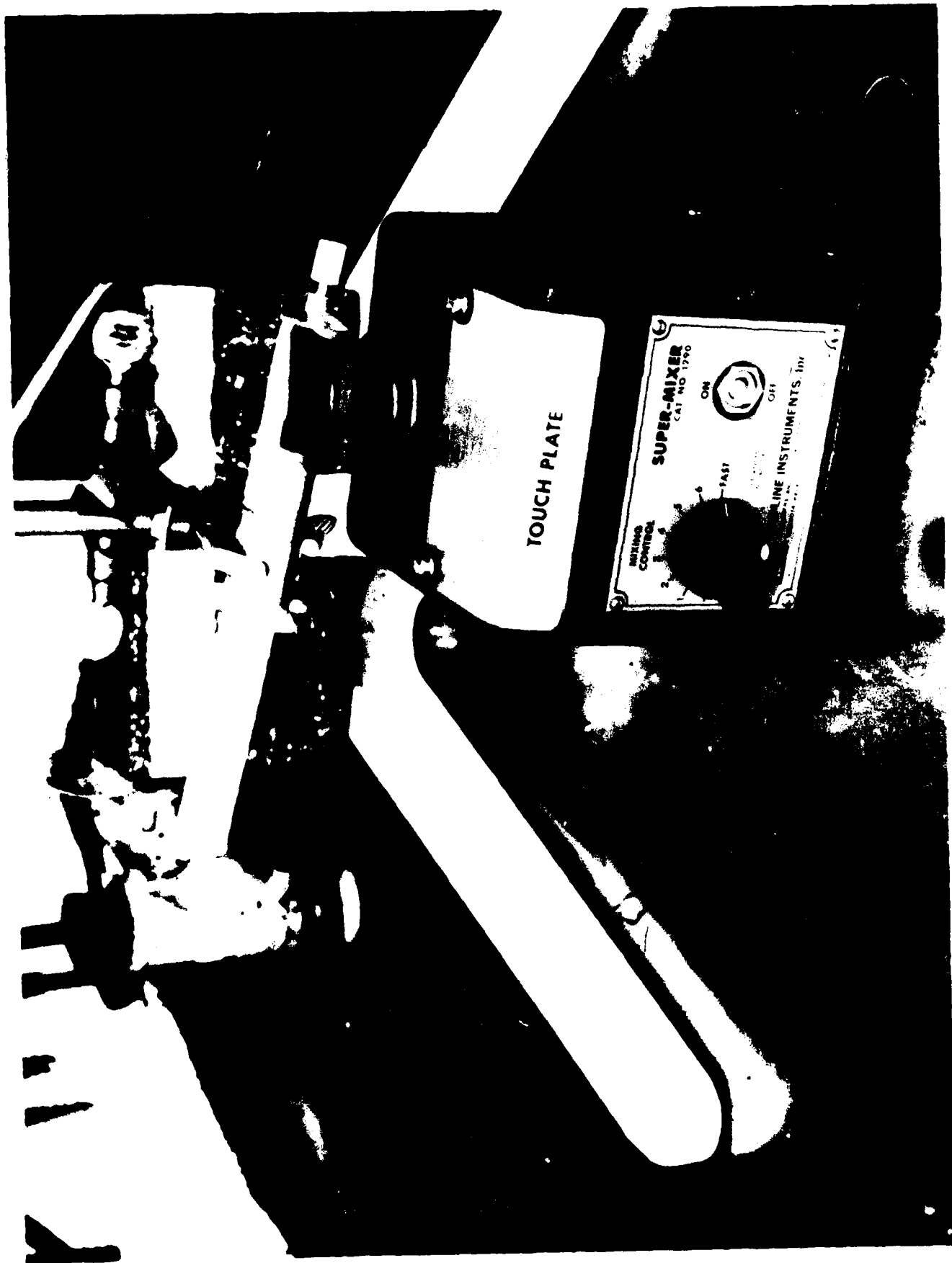


Fig. 6. Mixing hardware.

The paste was remotely mixed for 10 min using the super mixer. Midway through the mixing, the syringe was rotated 180° along axis. By vibrating the syringe in a vertical position with the tip up air pockets were removed from the paste and the paste was brought to a continuous column on the Teflon piston.

The syringe was mounted vertically in the syringe driver. The Teflon plug was removed from the syringe tip by attaching the plug to the overhead wire and remotely lowering the labjack under the syringe driver. Connections between the syringe and fill tube were made quickly. The cylinder vibrator was started and the syringe driver turned on. Flow of paste into the cylinder was monitored by observing bubbles coming from the overflow tube. The presence of paste in the overflow tube indicated that the cylinder was full. The filled cylinder was sealed by remotely welding shut both the fill and overflow tubes simultaneously. The cold weld tool was remotely removed from under the bomb lid.

The calorimeter bomb was closed remotely by lowering the lid with an air cylinder and using a hand operated probe to rotate the bomb to align the bolt holes. The motor driven socket was positioned over each bolt and lowered onto it with two air cylinders. The bolts were tightened until the motor stalled. The bomb is then considered safe for contact handling.

Cylinder Test Experiments

With the exception of the PFB and PFB/A1 experiments, all of the explosives were studied using standard cylinder test techniques.[8] PFB and PFB/A1 experiments were conducted in a shot chamber which allows only one streaking camera to be used and requires a xenon flash tube light source. In the standard technique as shown in Figure 7, a framing camera, two streaking cameras, and an argon candle-light source are used.

The copper cylinders employed in this test are machined to high precision and uniformity which contributes to a repeatability of $\pm 1\%$ in cylinder wall velocities. Approximate dimension of the standard cylinder are 25.4 mm (1 in.) ID, 2.6 mm (0.1 in.) wall thickness, and 305 mm (12 in.) length. Tests were performed in several scaled sizes.

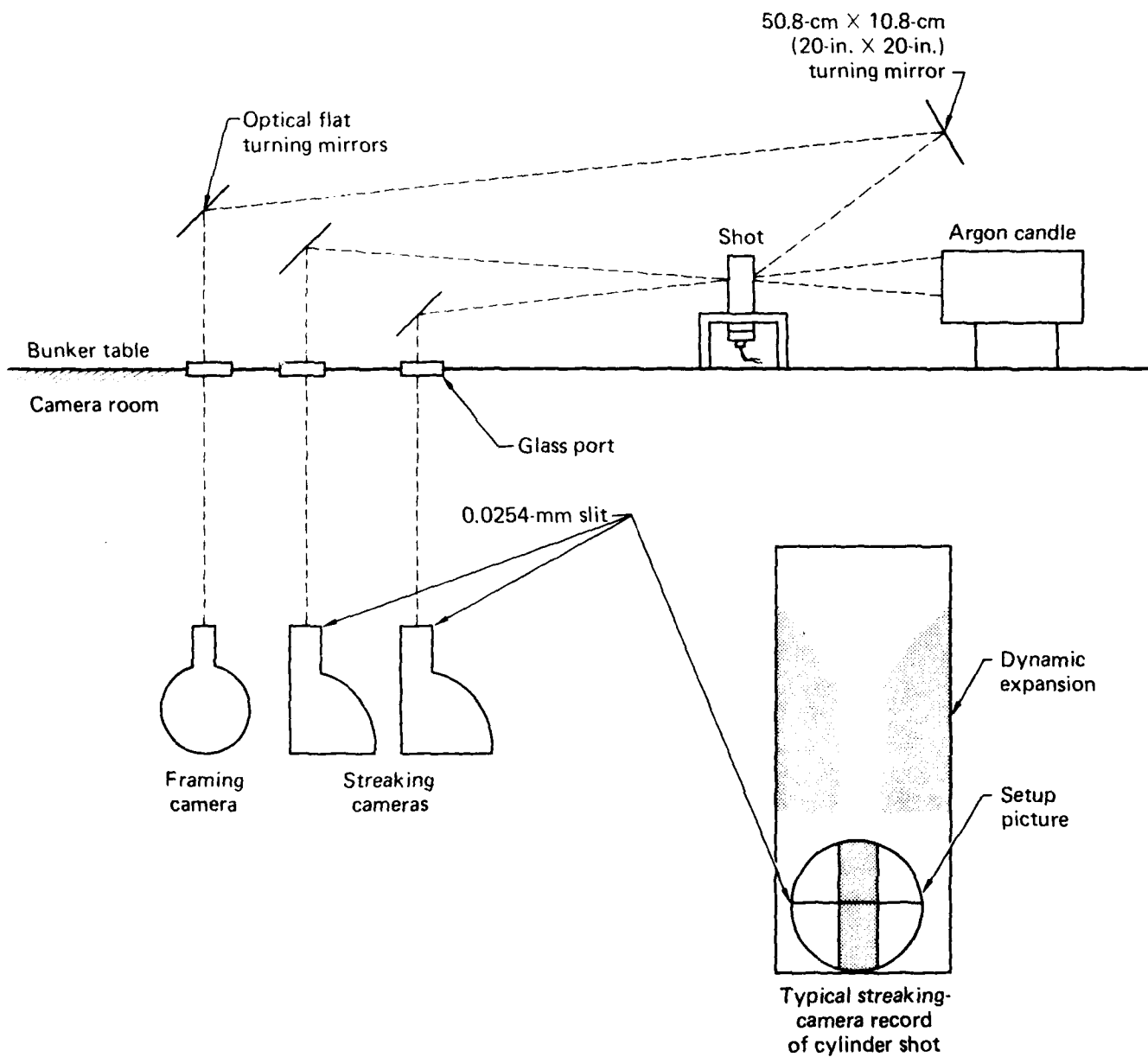


Fig. 7. Typical cylinder test configuration.

$$\text{i.e. } \frac{\text{MASS OF COPPER}}{\text{VOLUME OF EXPLOSIVE}} = \text{CONSTANT}$$

Wall velocities obtained in this manner are then scaled so that final velocities are those one would obtain if tests were performed in a standard size cylinder. This is allowed if one assumes that the explosives tested perform ideally in the geometries of interest.

Standard, and scaled half-, three quarters-, and double-size cylinders were used. Smaller sizes were required because of the limited supply of HNB and PFB.

The streaking camera records, Fig 7, are read with an optical comparator, digitized, and recorded on punch cards. Computer analysis gives wall velocity and time values as a function of radial expansion.

In order to suspend aluminum powders in TNM and PFB special mixers as shown in Figs. 8, 9, and 10 were fabricated for double and half size cylinders. The mixers were designed to maintain the aluminum in suspension prior to shot time, but to allow remote withdrawal of the mixing blade a few seconds before firing. The settling rate of 5 μ m aluminum powder was slow enough to allow adequate time to fire the shot before significant settling occurs. The aluminum powder consisted of 90% 5 μ m spherical aluminum and 10% 5 μ m flake aluminum. A small amount of flake aluminum was used because the thin cross section and air bubbles carried on the stearic acid coating help to get the aluminum reaction underway quickly. Flake aluminum is commonly used to sensitize commercial blasting agents.

TNM and aluminum powder were mixed together by hand prior to being placed in the copper tube. Because of TNM toxicity, protective equipment was used and the mixer was started remotely from the bunker. Because PFB and aluminum powder form a mixture which is highly impact sensitive, these components were placed in the shot tube individually and the mixer was required to complete the total mix remotely. The mixer was stopped and checked twice before the shot was fired.

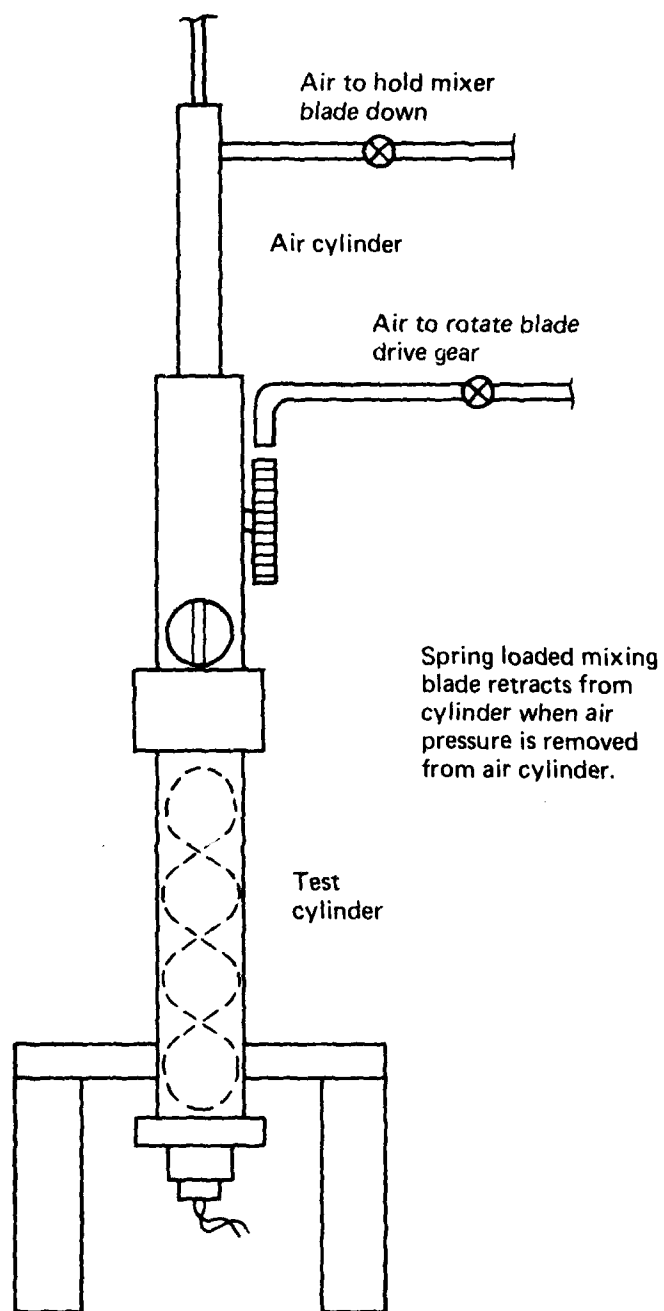


Fig. 8. Mixer to suspend aluminum in liquid explosives mounted in place on top of test cylinder.



Fig. 9. General view of 2" cylinder and mixer at firing bunker.

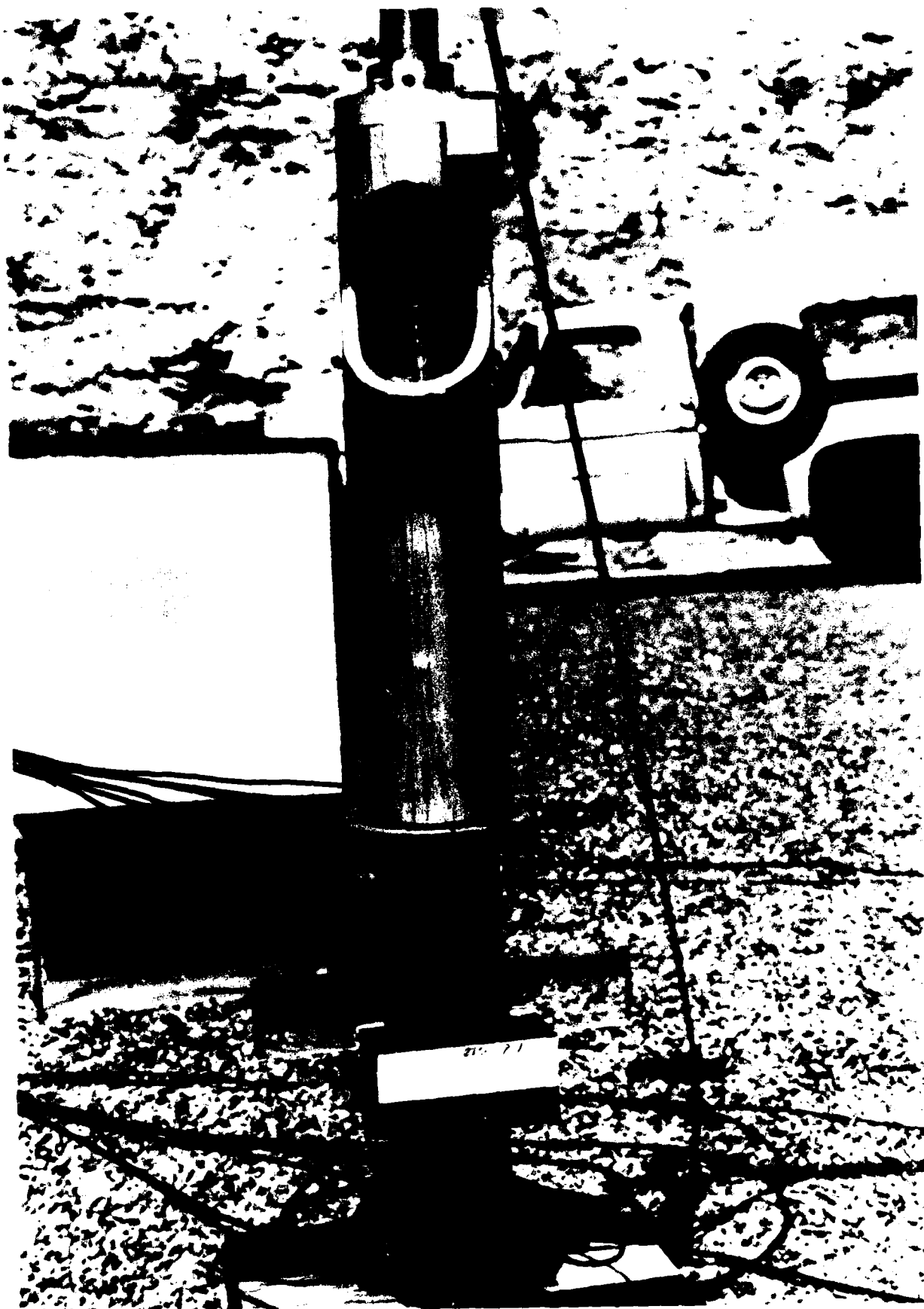


Fig. 10. Close up view of mixer and test cylinder.

RESULTS AND DISCUSSION

The results of these experiments are summarized in Table 2 and Figs. 11-14. A comparison of the individual pairs of detonation products shows clearly the advantages and disadvantages of fluorine as an oxidizing moiety in explosives. A further finding, shown graphically in Fig. 15 indicates that aluminum is essentially reacted to Al_2O_3 within the reaction zone of the detonating explosive and that the relative flatness of the expansion adiabats for products of aluminized explosives is due to very high vibrational energy (temperature) and consequently low γ , $[(d \ln P / d \ln v)_S]$.

H₂O vs. HF

RX-23-AB and 1,2-bis difluoramino propane (1,2-DP) give nearly the same number of moles of gas per gram of explosive. One, RX-23-AB, gives predominately H₂O while the other, 1,2-DP, gives mostly HF. If the different densities are considered, the RX-23-AB actually produces 1.36 times as much working fluid (0.0672 vs 0.0493 moles per cc) as the 1,2-DP. In spite of this, the cylinder test shows that the HF explosive (1,2-DP) outperforms the H₂O explosive at scaled expansions greater than $(R-R_0) = 10$ mm, about $3 V/V_0$ (Fig. 11). However, at early times ($V/V_0 < 2$) RX-23-AB is outperforming 1,2-DP. Although the comparison is possibly complicated by the existence of CF₄ as a detonation product of 1,2-DP before freeze-out, the effect of the higher detonation temperature can be seen as a late-time effect, i.e., decreases γ as a function of expansion at later (intermediate) expansion ratios. Comparison with nitromethane, a compound that produces both H₂O and carbon oxides as detonation products shows that the 1,2-DP compares favorably at early expansions and greatly outperforms it at later times.

Table 2. The Heats and Products of Detonation, Detonation Velocity and Calculated P_{CJ} and T_{CJ} .

Explosive	RX-23-AB (H ₂ O)	1,2-DP ^b (HF)	HNB (CO ₂)	PFB (CF ₄)	TNM/A1 (Al ₂ O ₃)	PFB/A1 ^c (AlF ₃)	TNM ^d
Density (g/cc)	1.38	1.27	1.918	1.64	1.828	1.76	1.65
%TMD	100-liq	100-liq	95.9	100-liq	95.5	96	100-liq
- ΔH Detonation (cal/g) exp.	1100 \pm 15	1435 \pm 50	1653 \pm 17	997 \pm 20	2773 \pm 28	2000	550
Detonation Vel. (mm/ μ sec)	7.48	5.96	9.35	4.35	6.01	4.82	6.31
TIGER calc P_{CJ} T_{CJ}	17.6 GPa 990K	17.5 GPa 3700K	35.4 GPa 4470K	8.8 GPa 3040K	14.2 GPa 8450K	14.6 GPa 5960K	14.0 GPa 2445K

Det. Products (Exp)
(moles/mole HE)^a

H ₂		0.45					
O ₂ or F ₂						0.23 F ₂	2.99 O ₂
H ₂ O	3.55						
HF		3.58					
CF ₄				0.887			
AlF ₃						0.82	
Al ₂ O ₃					0.60		
CO			0.27		0.12		
CO ₂			5.88		0.27		1.00
N ₂	1.27	1.14	2.96	0.382	0.63	0.28	1.99
C(s)		2.89		0.416		1.14	
Total Gas	4.82	5.31	9.11	1.27	1.02	1.33	5.98

a Trace Products (≤ 0.10 mole/mole HE) are not included.

b Detonation Products include 0.14 moles of methane (CH₄) per mole of HE.

c Heat and products corrected for water impurity in PFB. AlF₃ is assumed to be gaseous.

d Products calculated using BKWR-Equation of state in TIGER code.

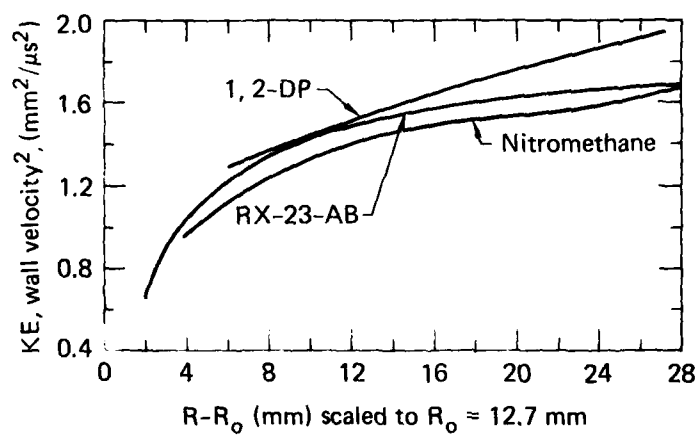


Fig. 11. Comparison of H_2O and HF as detonation products.

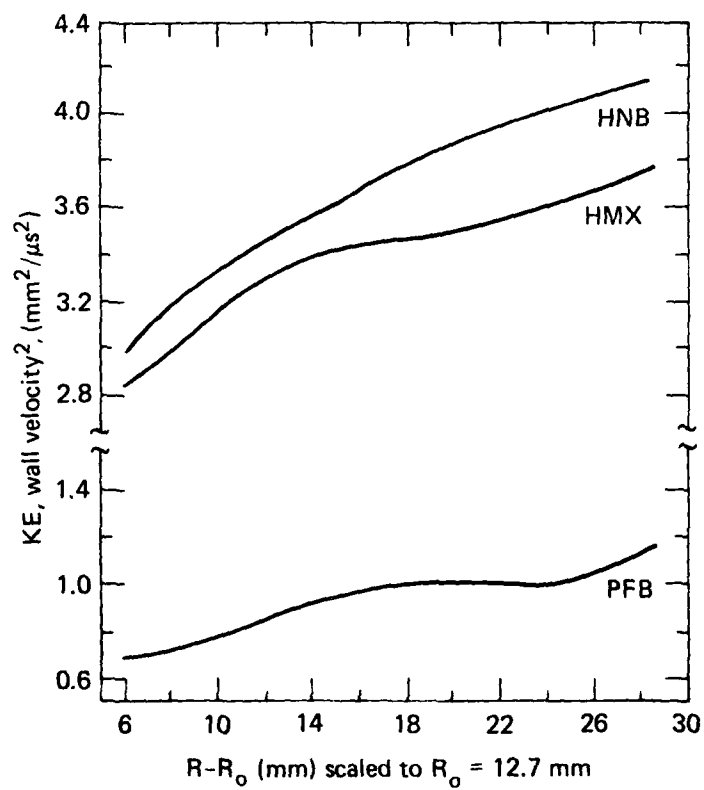


Fig. 12. Comparison of CO₂ and CF₄ as detonation products.

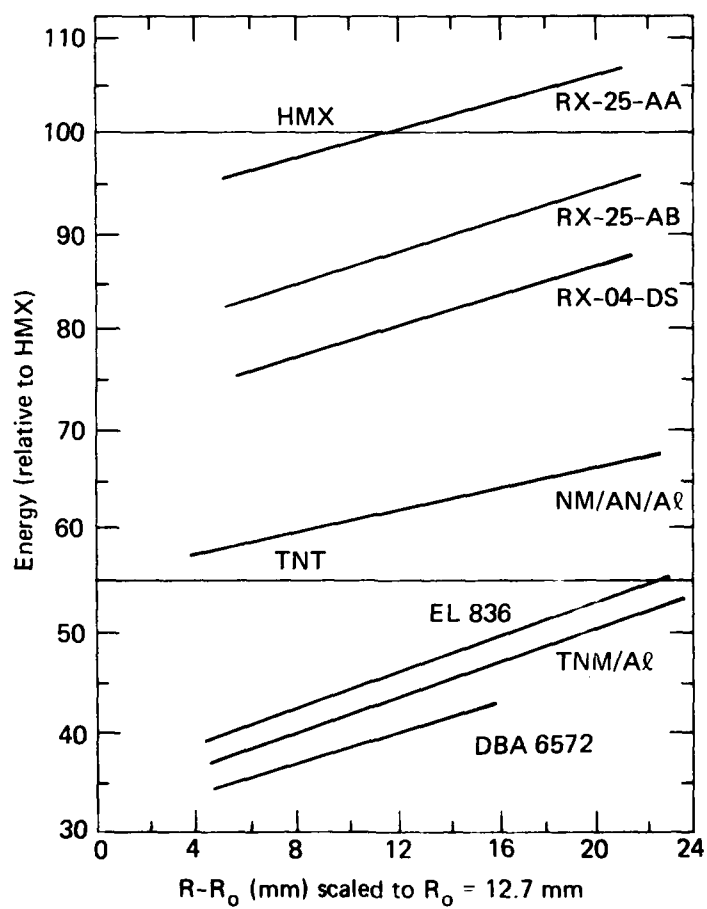


Fig. 13. Cylinder test energies of aluminized explosives (relative to HMX = 100).

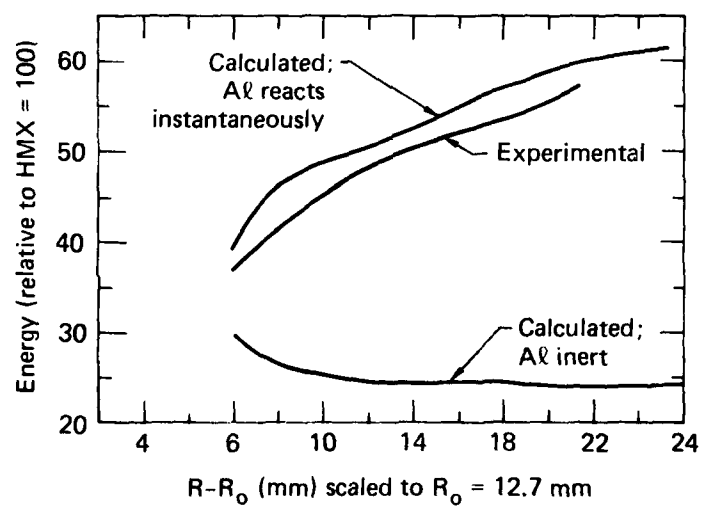


Fig. 14. Cylinder expansion of aluminized TNM compared to calculation.

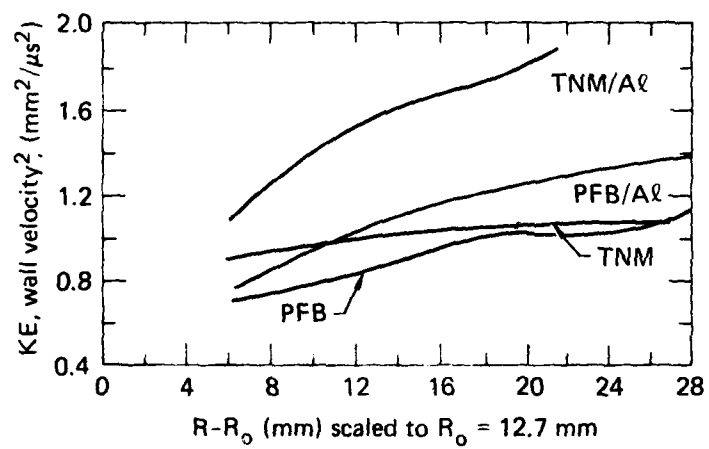


Fig. 15. Comparison of Al_2O_3 and AlF_3 as detonation products.

CO₂ vs. CF₄

Hexanitrobenzene (HNB) is an explosive which produces CO₂ and N₂ as detonation products almost exclusively. The mixture of bis- and tris-(difluoramino) perfluorobutanes (PFB) produces exclusively CF₄ and N₂ as gaseous products. Both materials give relatively high detonation temperatures. (Although the absolute values of detonation temperatures are unknown, the relative predicted values are taken as representative.) Because of the larger volume of gaseous products (0.05 moles/cm³ for HNB vs. 0.02 moles/cm³ for PFB), the higher density ($\rho = 1.92$ g/cm³ for HNB vs. 1.64 g/cm³ for PFB) and the higher energy ($-\Delta H = 1653$ cal/gm for HNB vs. $-\Delta H = 997$ for PFB) the CO₂ explosive outperforms the CF₄ explosive at all expansion ratios. In spite of this, the expansion isentropes for HNB and for PFB are essentially parallel (Fig. 12). If anything, the PFB isentrope is slightly flatter. This is in agreement with the larger number of internal degrees of freedom of CF₄ compared to CO₂.

Aluminized Explosives (Al₂O₃ vs. AlF₃)

Before proceeding with the discussion of Al₂O₃ and AlF₃ as detonation products, we must first eliminate the rate of aluminum reaction as a variable. Cylinder test data generated over the years on a variety of aluminized formulations strongly suggest that the aluminum is reacting similarly in all of these formulations. Figure 13 shows that the isentropes are nearly parallel in spite of large differences in aluminum loading and detonation energy. The expansion curves (i.e., the isentrope) are all much flatter than the curves for HMX or TNT with which they are compared.

We calculated the cylinder test expansion for an Al₂O₃-balanced mixture of aluminum and tetranitromethane using a BKWR equation of state and the TIGER code.[9] This type of calculation generally gives results which are more energetic than experiment for most explosives. This error is due principally to an improper treatment of attraction potentials in the equation of state. We reasoned that at the extremely high temperatures of detonation of the aluminized explosives and the lack of polar molecules in the detonation product would make attractive terms negligible, thus allowing the use of such an approach with little error.

The results of these calculations (Fig. 14) with the aluminum fully reacted at the C-J state closely match the actual cylinder test results. Both are significantly different from a calculation where the aluminum is inert but present as a thermal sink. These results, coupled with those shown in Fig. 13, indicate that the aluminum reacts very rapidly, i.e., reactions are complete near the C-J state. The delayed release of energy is a result of the high temperature of the detonation products, i.e., the high rotational and vibrational energy compared to the translational energy.

We then compared the results of the alumized tetranitromethane experiment with a cylinder test of a mixture of aluminum in PFB. These results are shown in Fig. 15. The addition of aluminum increased the performance of both TNM and PFB. In fact, the performance of the TNM was enhanced more significantly than that of PFB by the addition of aluminum. Calculations show that AlF_3 should be a gas at the predicted detonation temperature. However, because of the very high heat of vaporization of AlF_3 (72 kcal/mole or 93 kcal/mole to the dimer), the favorable energy release is not seen in the PFB/Al system.

CONCLUSIONS

Based on the available evidence, we must conclude that hydrogen fluoride is a favorable detonation product. This is especially true for applications requiring a longer, flatter pulse. However, the early energy (C-J pressure) is less than the comparable water-forming explosive of lower energy. It would seem, therefore, that some other species may be present in the early expansion of fluorinated explosives. This could be the CF_4 predicted by the TIGER code, but not experimentally observed, or some $(\text{HF})_n$ polymer. It would be worthwhile to investigate an HF-forming explosive without carbon.

The other two fluorinated products, CF_4 and AlF_3 , do not seem to be worth the trouble it takes to produce them.

The most important result of this work is the better understanding of the mechanism of reaction of small particle aluminum in a detonation.

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